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Crystal engineering of microporous 'Chinese-lantern' compounds to improve their ability to reversibly adsorb sulfur dioxide†

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Three new 'Chinese lantern' complexes [XMn(μ-dppO$_2$)$_4$MnX]$^{2+}$2X$^-$·4MeOH·Me$_2$CO [X = Cl, Br, I; dppO$_2$ = 1,3-bis(diphenylphosphinoyl)propane], have been structurally characterised using single-crystal X-ray diffraction and shown to have increasing affinity for SO$_2$ across the series Cl < Br < I *via* thermogravimetric measurements.

The discovery that dppO$_2$ and manganese isothiocyanate self-assemble to form 'Chinese-lantern' shaped macromolecules[1] (Fig. 1) emerged from research into the ability of manganese phosphine oxide complexes to capture sulfur dioxide within their lattices[2,3]

As our earlier work had shown that iodide containing monophosphine oxide compounds retained SO$_2$ more tenaciously than the corresponding isothiocyanates, dppO$_2$ complexes of manganese iodide, bromide and chloride were synthesised,‡ structurally characterised§ and subjected to SO$_2$ adsorption tests. At first sight all the lantern solids appear isostructural as they all crystallise in space group $I4/m$ and in each case the cations are centred on crystallographic C_{4h} sites. This leads to the structures having a characteristic microporous packing, criss-crossed by tunnels in the *a* and *b* directions (Fig 2).

The tunnels house counter-ions and, in the halide compounds, acetone and methanol guest molecules too. Although, reminiscent of zeolites, whose cages contain cations and water molecules, the tunnels are not rigid and cannot therefore act as molecular sieves. However, the dppO$_2$-based structures achieve steric control by a different means. Once complexed, the dppO$_2$ conformation is locked, as indicated by the near constancy of the torsion angles in all four compounds, Table 1. Effectively, the phenyl rings that surround each manganese atom, act as a rigid calixarene type well.

The molecular shape is maintained by non-classical CH/π hydrogen bonds[4] between phenyl rings on adjacent dppO$_2$ ligands in the lantern cations. These type of bonds are also a feature of the crystal packing (Fig 2) and hence a reason for the four crystal structures being nearly identical.

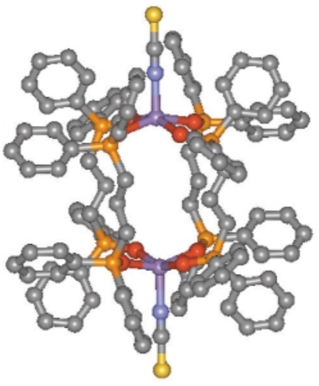

Fig. 1 The cation from [Mn$_2$(μ-dppO$_2$)$_4$(NCS)$_2$]$^{2+}$ 2(NCS)$^-$ **1**.

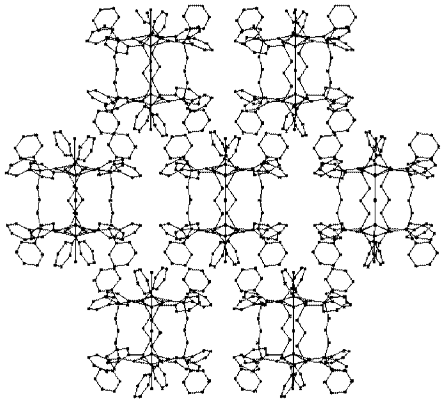

Fig. 2 Crystal packing of the lantern shaped cations, viewed down the crystallographic *b* axis.

Despite the above similarities, closer examination of the manganese and halide atoms lying along the central four-fold axis reveals striking differences between the structures. Importantly, halide anions are smaller than thiocyanate and can be accommodated within the lantern shaped central part of the complex (Cl 100%, Br 100%, I 44%). This difference has ramifications for the manganese atom, which can now occupy two types of sites *ca.* 0.5 on either side of the plane defined by the four coordinated oxygen atoms. This allows an Mn–X bond to form to the central halide atom or, alternatively, to the external capping halide (Table 1).

Table 1 Torsion angles ϕ(°) relative to P=O and Mn displacement from the oxygen plane[a]

				Mn displacement/Å	
Anio	ϕ_1	ϕ_2	ϕ_3	In	Out
NCS	−24.0	9.3	−62.9	—	0.47
C	−26.7	11.2	−68.1	−0.61	0.46
Br	−25.7	13.2	−71.7	−0.59	0.48
I	−23.9	12.6	−69.1	−0.44	0.59

[a] ϕ_1 and ϕ_2 = O=P–C–C$_{\mathrm{Ph}}$, ϕ_3 = O=P–C–C$_{\mathrm{prop}}$.

These features are manifested in the Cl$^-$ and Br$^-$ X-ray structures as two semi-populated manganese sites and a semi-populated external capping halide site. This leads to the straightforward interpretation that a racemic mixture of the C_4 symmetry molecule illustrated in Fig. 3 occupies each molecular site.

The structures are completed by halide counter-ions, each flanked by two methanol solvate molecules, and disordered acetone, occupying C_{4h} sites above the capping halide ligands. In the halide cases this lead to a total formulation of [Mn$_2$(μ-dppO$_2$)$_4$X$_2$]$^{2+}$2X$^-$·Me$_2$CO·4MeOH.

As the iodide central site is not fully occupied [44.3(1)%], presumably because of the bulk of I$^-$, it is tempting to assume that the molecular site contains a mixture of isothiocyanate and chloride type complexes. However a reasonable match for the crystallographically derived site occupancies cannot be ob-

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† Electronic supplementary information (ESI) available: full synthesis and crystal refinement details for **2**–**4**. See http://www.rsc.org/suppdata/cc/b1/b101263k/

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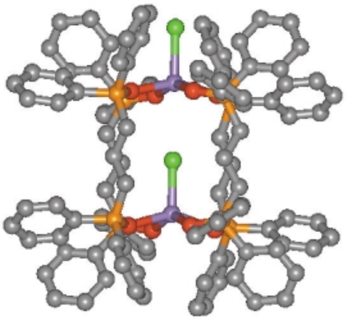

Fig. 3 The cation from $[Mn_2(\mu\text{-}dppO_2)_4Cl_2]^{2+}2Cl^{-}\cdot Me_2CO\cdot 4MeOH$ **2**, which is isostructural with the bromide analogue **3**.

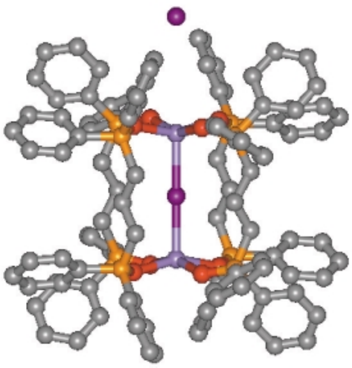

Fig. 4 The cation from $[Mn_2(\mu\text{-}dppO_2)_4I_2]^{2+}$ $2I^{-}\cdot Me_2CO\cdot 4MeOH$ **4**, showing the central centrosymmetric iodine atom.

tained using this model and 30% of a third molecular configuration must also be used (Fig. 4).

The manganese bonded to the externally capping iodide has flipped to the inner site, allowing the central iodide to bridge the two manganese atoms. This breaks the bond to the capping iodide, which is now held in position by dispersive forces within the calixarene well.

The ability of manganese to occupy the two types of sites is reminiscent of iron in haemoglobin, but the dynamic haemoglobin situation and static disorder cannot be distinguished crystallographically. Nevertheless, a guest molecule diffusing through the microporous tunnels in the iodide crystals would encounter an additional halide bridged Mn type of calixarene site, compared to only the non-bridged types in the bromide and chloride structures.

A series of combined thermogravimetric and X-ray powder diffraction experiments were therefore carried out in order to measure the effect of the above structural variations on SO_2 adsorption. A typical curve shows rapid and fully reversible SO_2 take-up, reminiscent of zeolites. The XRD patterns confirm that all the compounds retain their original crystal structure, although small expansions of the unit cells were observed on adsorption ($<3\%$ at maximum of 4 SO_2 molecules /lantern). Analysis of the isotherms using Hill's adaptation of Langmuir's theory provided a series of equilibrium constants, which were then used to determine the enthalpies of adsorption by means of the Van't Hoff equation. The enthalpy values obtained for the chloride, bromide, iodide and isothiocyanate lanterns were -34, -44, -54 and -39 kJ mol^{-1}, respectively.

As would be expected for compounds that adsorb SO_2 so readily, the energies straddle the physisorption/chemisorption boundary.[5] They are comparable in value to the -50 kJ mol^{-1} determined for $[K(18\text{-crown-}6)]^{+}[NCS\cdot SO_2]^{-}$ [5] and fall in the range -20 to -79 kJ mol^{-1} calculated for a series of iodosulfinates, $[I\cdot SO_2]^{-}$.[6] The order $Cl < Br < I$ is the same as was found in square-planar $Ir(X)(CO)(PPh_3)_2$ complexes,[8,9] where the SO_2 binds loosely to the halide atom, suggesting that this type of interaction also influences the retention of SO_2 within the lantern crystals.

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Notes and references

‡ Synthesis of $[Mn_2(\mu\text{-}dppO_2)_4X_2]X_2\cdot Me_2CO\cdot 4MeOH$ **2**–**4**. MnX_2 (1 equiv.) and $dppO_2\cdot H_2O$ (2 equiv.) were stirred together in acetone–methanol (1 : 1) for **2** and **3** and diethyl ether for **4**. The resulting solid was filtered off under suction, washed with diethyl ether and dried *in vacuo*.

Crystals of **2** and **3** were grown by the vapor diffusion of diethyl ether onto an acetone–methanol (1 : 1) solution of the synthesized complex, and by liquid diffusion using the same solvents for **4**.

TGA measurements were carried out by means of a CAHN TG-131. Exhaust gases from this instrument were fed to an enclosed powder sample in a Scintag XDS2000 X-ray powder diffractometer for simultaneous TGA/XRD analysis.

§ *Crystal data*: for **2**: $C_{115}H_{126}O_{13}P_8Mn_2Cl_4$, tetragonal, space group $I4/m$, $a = b = 14.382(3)$, $c = 26.076(9)$ Å, $V = 5393(2)$ Å^3, $T = 223$ K, $\mu = 5.14$ cm^{-1}, $Z = 2$, 2441 unique ($R_{\text{int}} = 0.053$), $wR2 = 0.152$ for all reflections and $R1 = 0.070$ for 1321 reflections $[I > 2\sigma(I)]$.

For **3**: $C_{115}H_{126}O_{13}P_8Mn_2Br_4$, tetragonal, space group $I4/m$, $a = b = 14.523(4)$, $c = 25.874(12)$ Å, $V = 5457(3)$ Å^3, $T = 223$ K. $\mu = 18.74$ cm^{-1}, $Z = 2$, 2750 unique, $wR2 = 0.158$ for all reflections and $R1 = 0.073$ for 1500 reflections $[I > 2\sigma(I)]$.

For **4**: $C_{115}H_{126}O_{13}P_8Mn_2I_4$, tetragonal, space group $I4/m$, $a = b = 14.984(4)$, $c = 25.761(12)$ Å, $V = 5784(3)$ Å^3, $T = 223$ K, $\mu = 14.55$ cm^{-1}, $Z = 2$, 4499 unique ($R_{\text{int}} = 0.079$), $wR2 = 0.100$ for all reflections and $R1 = 0.041$ for 2103 reflections $[I > 2\sigma(I)]$.

CCDC reference numbers 153090-153092. See http://www.rsc.org/suppdata/cc/b1/b101263k/ for crystallographic data in CIF or other electronic format.

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